# A COMPARISON OF ANCIENT AND MODERN SEQUOIA WOOD

Paul F. Cundy

When wood remains buried for extremely long periods of time without losing its fibrous or "woody" character, some very interesting changes take place in its structure and chemical constitution. These changes are shown quite strikingly when the ancient wood is compared with a modern specimen of the same species. In the present instance the comparison has been made between a fossil wood believed to be an ancient form of *Sequoia gigantea* and a specimen of modern Big Tree, *Sequoia gigantea* Decaisne. The fossil wood was unearthed in a bed of Miocene gravel in a mine tunnel in Eldorado County, California, where, it has been estimated, it lay buried thirty million years. The gravel bed, located about a mile from the mouth of the tunnel, is overlaid with eight hundred feet of lava and is part of the bed of an ancient stream. The modern specimen is from Whitaker's Forest in Tulare County, California.

Except for the fact that the ancient wood has a dark brown color and some pieces are twisted and bent, it appears, superficially, to be much like normal wood. In contrast to the modern wood, however, it is quite soft and friable. Most of the pieces may be pulled apart by hand and the fragments thus separated reduced to the size of very coarse sawdust by rolling them firmly between the fingers. Similar characteristics have been noted by other investigators of fossil woods (6).

The structure of the ancient wood resembles very closely that of modern Big Tree wood (pls. 17, 18). The wide band of large thin-walled springwood tracheids makes an abrupt transition to the narrow band of flattened thick-walled summerwood tracheids. The tracheids have bordered pits on the radial walls in one or two rows and smaller bordered pits on the tangential walls in the last few rows of summerwood cells. The pits leading to the ray parenchyma are fairly large, quite uniform in size, and usually oval; there are one to five (generally two) pits per ray crossing. The rays are uniseriate or occasionally in part biseriate, consisting entirely of ray parenchyma cells, and range up to thirty-one cells (800 μ) in height. There are approximately five rays per millimeter tangentially on the transverse section and fifteen to twenty per square millimeter on the tangential surface. The longitudinal parenchyma are metatracheal-diffuse (there seem to be fewer than in the modern wood) and are located chiefly in the summerwood zone. Although normal resin canals are absent, a short tangential row of traumatic (wound) canals is present; these occur occasionally in *Sequoia gigantea*. It is apparent from the

Corrected date line: Madroño, Vol. 8, pp. 105–144. November 5, 1945.
Madroño, Vol. 8, pp. 145–176. January 30, 1946.

photomicrographs that many of the cells of the ancient wood have been distorted; in fact, they are almost collapsed in certain areas.

The modern wood was reduced to sawdust, using a power saw with a box for retaining the sawdust; the ancient material was picked apart by hand, with the occasional aid of a knife, and crushed by rolling between the fingers. Both samples were further reduced in a Wiley mill to wood meal passing the forty-

Table 1. Chemical Analysis of Ancient and Modern Sequoia Wood. (All calculations are on the basis of ovendry, unextracted wood.)

| | Ancient, per cent | Modern, per cent |
|---|---|---|
| Ether solubility | 0.33 | 0.74 |
| Alcohol solubility | 1.36 | 12.13 |
| Hot-water solubility | 1.71 | 3.10 |
| Total extractives | 3.4 | 16.0 |
| Ash | 1.98 | 0.77 |
| Lignin | 57.1 | 33.5 |
| Methoxyl of lignin | 13.66 | 13.63 |
| Pentosans | 4.0 | 12.3 |
| Uronic anhydride ($CO_2 \times 4$) | 1.72 | 4.68 |
| Cross and Bevan cellulose | 38.2 | 37.3 |
| Alpha-cellulose (determined on Cross and Bevan cellulose) | 26.4 | 29.1 |
| Viscosity of Cross and Bevan cellulose | 6.2 cp. | 23.6 cp. |

mesh sieve. Extractives and ash were determined on the original unextracted wood meal. The extracted wood used for the other determinations was prepared by subjecting a large portion of wood meal to a treatment analogous to that used in the determination of the extractives present in the unextracted wood. This treatment is described later. For the determination of Cross and Bevan cellulose, the fraction of the wood meal which passed the forty-mesh sieve but was retained on the sixty-mesh sieve was used; in all other determinations, the whole wood meal passing the forty-mesh sieve was used.

The ether and alcohol solubilities were determined by extracting the wood meal, successively, eight hours with ether and sixteen hours with 95 per cent ethyl alcohol in a Soxhlet extractor. The hot water solubility was determined by heating water suspensions of this extracted wood meal in a hot water bath for three one-hour periods. The lignin, methoxyl of the isolated lignin, and the alpha-cellulose and viscosity of the Cross and Bevan cellulose were determined by TAPPI standard methods (7). Cross and Bevan cellulose was determined by a modification of the Forest Products Laboratory procedure (2), the principal difference being that the wood meal, after being chlorinated, was heated four minutes instead of thirty minutes with 2 per cent sodium sulfite solution. Pentosans were determined by distillation with 12 per

cent hydrochloric acid followed by precipitation with phloroglucinol (1). Uronic anhydrides were determined by a modification of the method of Burkhart, *et al.* (3); the principal change involved heating the hydrochloric acid suspension of the wood fifteen minutes at a temperature of 70° centigrade to remove carbonate $CO_2$ before the absorption tube was attached.

In contrast to the experience of other investigators (4, 5, 6) no difficulty with gelatinization was encountered in the preparation of Cross and Bevan cellulose from the ancient wood. The delignification proceeded much more rapidly than did that of the modern specimen. The results of the analyses are shown in Table 1.

If the composition of the woods is compared on the whole wood basis, it will be noted that there have been marked decreases in extractives, pentosans, and uronic anhydride in the ancient wood, and a large increase in lignin. Cross and Bevan cellulose appears to be practically unchanged.

The greatest differences in composition are in lignin, which apparently increased, and extractives (particularly alcohol extractives), which decreased. The increase in lignin content is particularly intriguing. It is conceivable that extractives might, upon aging, become insoluble in 72 per cent sulfuric acid, as well as in the usual solvents, and be isolated with the lignin, thereby accounting for some of the increase in the latter. However, the remarkable similarity of the methoxyl content of the lignin isolated from the two woods makes this assumption untenable because the methoxyl content of the extractives is much lower than that of lignin. Since the alcohol-soluble portion would be partially water-soluble as well, it is more likely that most of the extractives have been lost. Therefore, to explain the increased lignin content, it must be assumed that lignin is more resistant to deterioration than are any of the other major constituents of wood and thus appears to increase in quantity because the other constituents are lost so much more rapidly, a suggestion which has been made by other investigators.

If the further assumption is made that none of the lignin has been lost, the basis is provided for a more rational comparison of the two woods. In other words, if it is assumed that instead of 57.1 per cent, the lignin content of the ancient wood was originally the same as that shown by the modern wood (33.5 per cent) and no lignin was lost, 58.7 per cent $[(33.5/57.1) \times 100]$ of the original wood remains and the other analyses should be adjusted accordingly. Although it is impossible to say how nearly correct this assumption may be, it furnishes the only logical basis of comparison. Jahn and Harlow (5) found that, in ancient beechwood, the loss in weight as calculated from the increase in lignin, assuming no loss of lignin, agreed almost exactly with the loss in weight as calculated from apparent density measurements. This would

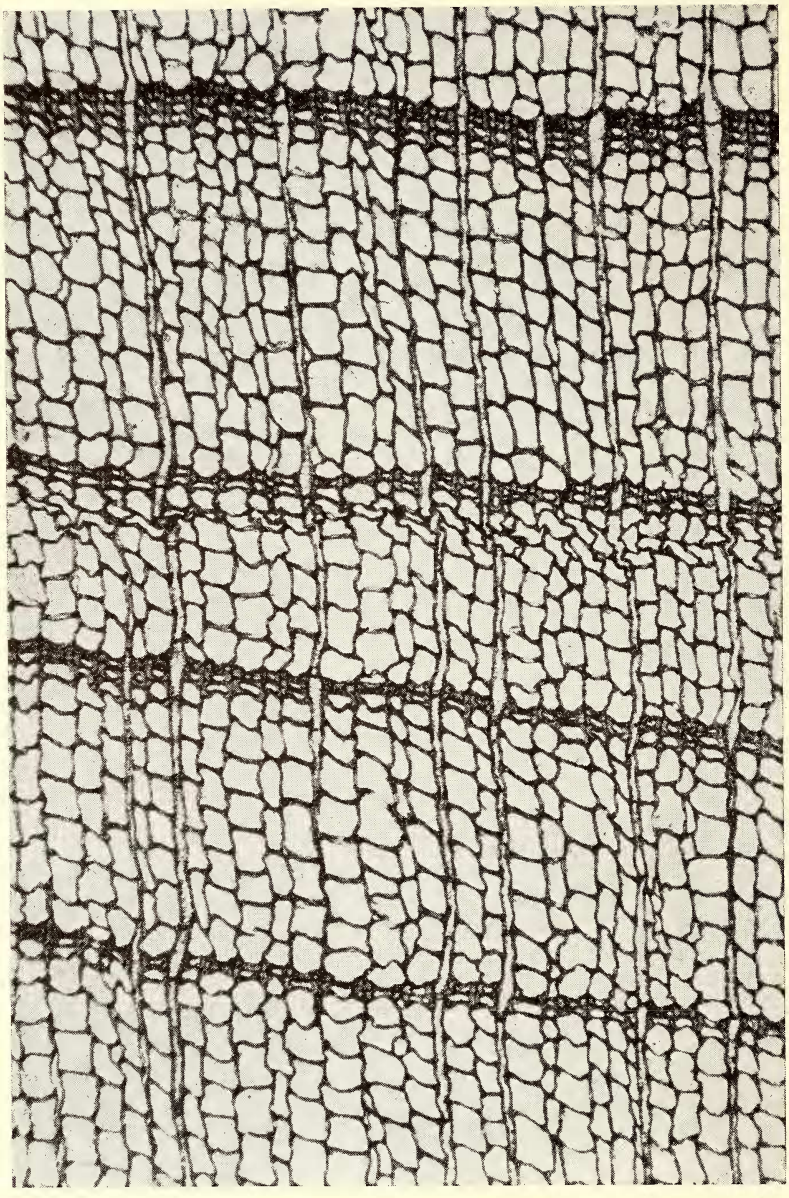

PLATE 17. STRUCTURE OF ANCIENT WOOD, ×100.

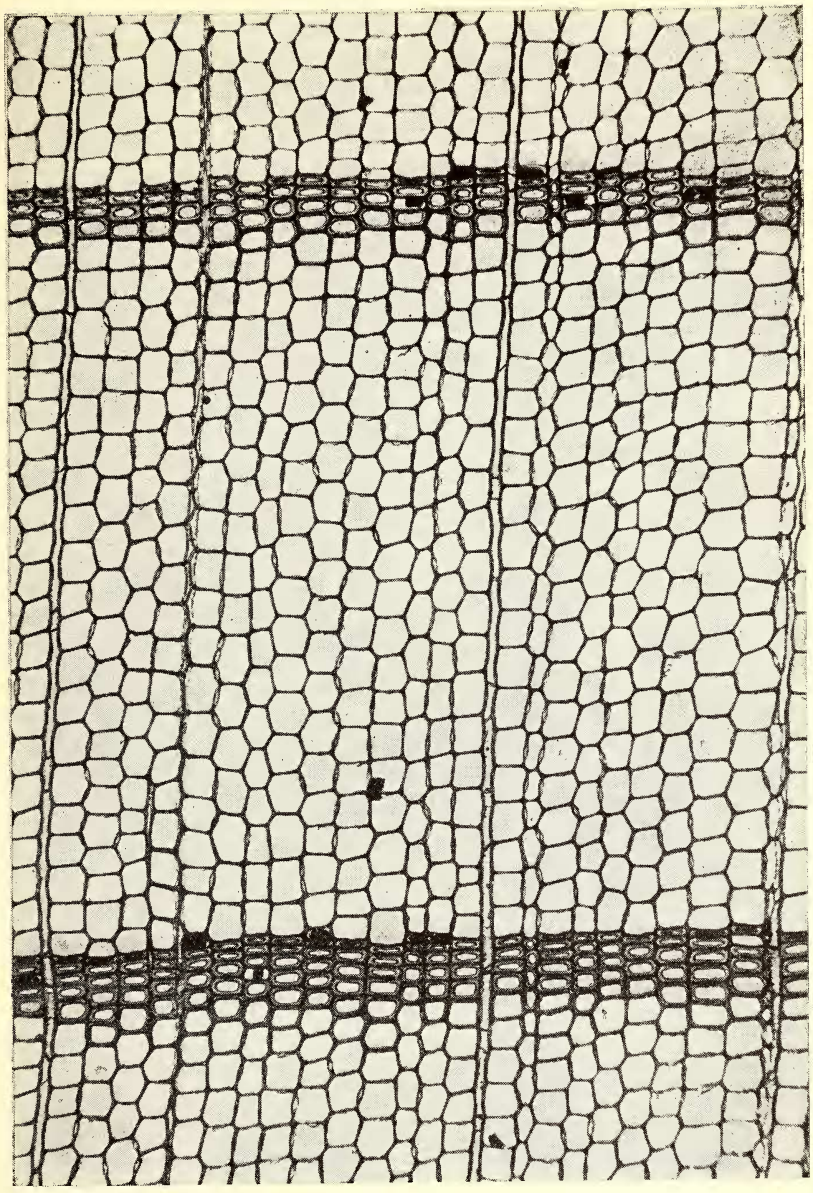

PLATE 18. STRUCTURE OF SEQUOIA GIGANTEA, × 100.

indicate that, in this case, there had been neither a loss nor an accumulation of lignin. In an attempt to provide such an independent check in the case of the sequoia wood, density measurements were made on both samples. Small rectangular blocks of the woods, dried to constant weight, were dipped in hot paraffin, and then weighed in and out of water, weighting the wood sufficiently to overcome its tendency to float. The weight of water absorbed by the wood during the period of immersion necessary to complete a weighing was negligible.

On the ash-free basis, the apparent densities of the ancient and modern samples are, respectively, 0.222 and 0.323. These

Table 2. Adjusted Chemical Analysis of Ancient Wood

| | Basis—Wood of normal lignin content, per cent | Loss—Basis, normal wood, per cent |
|---|---|---|
| Extractives | 2.00 | 87.5 |
| Ash | 1.16 | 33.6* |
| Cross and Bevan cellulose | 22.4 | 39.9 |
| Alpha-cellulose | 15.5 | 46.7 |
| Pentosans | 2.3 | 81.3 |
| Uronic anhydride ($CO_2 \times 4$) | 1.01 | 78.4 |

* Gain.

results were confirmed by calculations made from actual measurement of the dimensions of the blocks. Using these density values, it would appear that 68.7 per cent of the original wood remains, as compared with 58.7 per cent as calculated from the gain in lignin. From this, it might be concluded that some lignin has accumulated in the aging process but, as previously mentioned, the methoxyl content of the two lignins lends little credence to this view. At least part of the discrepancy might be explained by assuming that the pressure of the lava and other overburden has had a compressing effect on the ancient wood, thereby increasing its apparent density. An examination of the cell structure of this wood (plate 17) shows cell deformation amounting, in some cases, almost to collapse. Such a change would, of course, increase the apparent density of the wood and lead to a fictitiously low value for the loss in weight as calculated from the decrease in apparent density.

Thus, although density measurements do not confirm the assumption that lignin is neither lost nor accumulated, neither do they interpose any serious objections to its use as a basis for calculation. It need hardly be pointed out, of course, that the one basic assumption upon which all these comparisons are made can never be affirmed—namely, that the modern wood has the same chemi-

cal and physical constitution as did its ancient prototype in its original state.

In the first column of Table 2 is shown the composition of the ancient wood adjusted to conform to the assumption that no lignin has been lost and, accordingly, that 58.7 per cent of the original wood remains. The second column shows the percentage difference from the composition of modern big tree wood.

When this basis of comparison is used, it appears that only about 12 per cent of the original extractives and 20 per cent of the pentosans and uronic anhydrides of the ancient wood remain, as compared with a retention of about 55–60 per cent of the cellulose. The loss of so-called hemicelluloses is, in other words, approximately twice as great as that of cellulose, a point which is not too surprising because they represent, principally, molecules of a lower degree of polymerization than cellulose. There is some evidence, however, that the cellulose suffered greater deterioration during burial than is indicated by the percentage loss shown in Table 2. Alpha-cellulose and viscosity measurements made on Cross and Bevan cellulose from the ancient wood showed losses of 12.7 and 73.3 per cent, respectively, from the values of corresponding measurements made on Cross and Bevan cellulose from the modern wood, despite the fact that a greater number of chlorinations were required to delignify the modern wood. This suggests that what cellulose remains in the ancient wood possesses a considerably lower degree of polymerization than it did originally. The increase in ash content, which is found in all woods which have been buried for long periods of time, is to be expected. No evidence of petrification was found.

Grateful acknowledgment is made to Professor Emanuel Fritz, of the Department of Forestry at the University of California, who obtained the samples of the two woods and to the Pacific Lumber Company who made them available to this laboratory. Especial thanks are due Dr. I. H. Isenberg who prepared the sections of the wood, examined them microscopically, and provided the portion of the description which relates to that examination, and to Dr. B. L. Browning who made valuable suggestions regarding the analytical work. Thanks are also due Miss Eda Nihlen for preparing the photomicrographs and Miss Virginia West for making the viscosity measurements.

The Institute of Paper Chemistry,
Appleton, Wisconsin.

## Literature Cited

1. Association of Official Agricultural Chemists. Methods of analysis. 5th ed., p. 361. 1940.
2. Bray, M. W. Methods used at the Forest Products Laboratory for the chemical analysis of pulps and pulpwoods, 1939: 12–13. 1939.
3. Burkhart, B., L. Baur, and K. P. Link. A Micromethod for the determination of uronic acids. Jour. Biol. Chem. 104: 171–181. 1934.

4. Gortner, W. A. Analysis of glacial and preglacial woods. Jour. Am. Chem. Soc. 60: 2509. 1938.
5. Jahn, E. C., and Wm. M. Harlow. Chemistry of ancient beech stakes from the fishweir. Papers Robt. S. Peabody Foundation Archeol. 2: 90–95. 1942.
6. Mitchell, R. L., and G. J. Ritter. Composition of three fossil woods from the Miocene auriferous gravels of California. Jour. Am. Chem. Soc. 56: 1603. 1934.
7. Technical Association of the Pulp and Paper Industry. Tentative and official testing methods.

## NOTES ON TRIFOLIUM ERIOCEPHALUM NUTTALL

James S. Martin

During a recent taxonomic study of the native clovers of the United States, several nomenclatural ambiguities were discovered. Two varieties of *Trifolium eriocephalum* Nuttall long have been known under invalid names and the distinctions between the several varieties never have been very clear-cut. The species and its four varieties are revised here in an attempt to correct these difficulties. Herbarium material from the following institutions has been studied: University of California, Berkeley, California; Dudley Herbarium, Stanford University, California; Gray Herbarium, Harvard University, Cambridge, Massachusetts; New York Botanical Garden, New York, New York; Pomona College, Claremont, California; Philadelphia Academy of Sciences, Philadelphia, Pennsylvania; Utah State Agricultural College, Logan, Utah; University of Washington, Seattle, Washington. I am deeply grateful to the curators of these herbaria for the loan of their material.

Trifolium eriocephalum Nutt. in Torrey and Gray, Fl. N. Am. 1: 313. 1838.

Usually villous or rarely glabrous perennials; stems branching from apex of thick, deep root, erect or spreading, 5–45 cm. tall, 1–3 mm. in diameter; leaflets always 3, varying in shape; inflorescence 25–85-flowered, 15–30 mm. in diameter, without an involucre, the pedicels less than 0.8 mm. long, the entire inflorescence often horizontal or sometimes inverted because of the bending of the peduncle just beneath the head; flowers yellowish, pink, purplish or ochroleucus, 8–16 mm. long, sharply reflexed, the curvature sharp near the base; calyx somewhat shorter than the banner, the tube 1–3 mm. long, membranous, strongly 10(9–11)-veined, teeth slenderly subulate, sharp but not spine-tipped, often curved and twisted, usually villous with long diverging hairs 0.7–2.5 mm. long, the lower teeth 2–5 times as long as the tube, the upper teeth subequal to or shorter than the lower; banner ovate, oblong,